PH102, 2013W, Lecture Notes: January 22, Tues, Class 5

Invariance and Conservation, orbital and spin angular momentum quantization, LS coupling, and Periodic table

Objectives:

- Determine translational and rotational invariance and corresponding linear and angular momentum conservation for a given Hamiltonian of a system.
- Define what the Spin angular momentum represents and how it is quantized.
- Define the total angular momentum, how it is quantized, and how it is related to L and S.
- Understand what LS coupling represents and how it is done.
- Understand Pauli exclusion principle and apply it to bosons and fermions
- Recognize patterns in the periodic table and connect them to underlying causes.

……

Invariance and Conservation

The translation invariance means that the Hamiltonian is translationally invariant. The rotational invariance means that the Hamiltonian is rotationally invariant.

> The formal definition of the translational invariance is that $H(x, y, z) = H(x + a, y + b, z + c)$ for any constants a, b, c, where x, y, z are the Cartesian coordinates. The formal definition of the rotational invariance is that $H(r, \theta, \phi) = H(r, \theta + a, \phi + b)$ for any constants a, b, where r, θ, ϕ are spherical coordinates.

First, note that

> H = T (kinetic energy) + U (potential energy).

The kinetic energy is both translationally and rotationally invariant.

The potential energy is translationally invariant if it is independent of x, y, z when it is expressed as a function of the Cartesian coordinates, x, y, z. (If the potential is independent of a certain Cartesian coordinate only, then the system is partially translationally invariant.)

The potential energy is rotationally invariant if it is independent of θ, ϕ, when it is expressed as a function of the spherical coordinates, r, θ, ϕ. (If the potential is independent of one angle only (like ϕ), then the system is partially rotationally invariant.)

It the system is translationally invariant, then the momentum is conserved. In QM, this means that the Hamiltonian eigenstate can be written as a momentum eigenstate (e^{ikx} for example).

If the system is rotationally invariant, then the angular momentum is conserved. In QM, this means that the Hamiltonian eigenstate can be written as an angular momentum eigenstate ($Y_{lm}(\theta, \phi)$ or $e^{im\phi}$).

Let's compare Hamiltonian operators for a particle in a 3d infinite box and for an electron in the hydrogen atom.

Schrodinger Equation: $\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) + U(\vec{x})\psi(\vec{x}) = E\,\psi(\vec{x})$

Hamiltonian: $H = \frac{-\hbar^2}{2m}\nabla^2 + U(\vec{x})$

For the 3d Infinite box $U(\vec{x}) = \begin{cases} 0 & 0 < x < L_x, 0 < y < L_y . 0 < z < L_z \\ \infty & otherwise \end{cases}$

For the hydrogen atom $U(r) = \frac{1}{4\pi\varepsilon_0}\frac{-e^2}{r}$

3d infinite box:

Potential is dependent on position of the box, so the Hamiltonian of the system is not invariant under translation moving in any one of three directions, x, y, z.

Since

$\begin{cases} x = rcos\phi\ sin\vartheta \\ y = r\sin\phi\cos\theta \\ \quad z = rcos\theta \end{cases}$ the box potential is not invariant under rotation.

This means that the linear momentum and the angular momentum of a particle moving inside the 3d box will not be conserved.

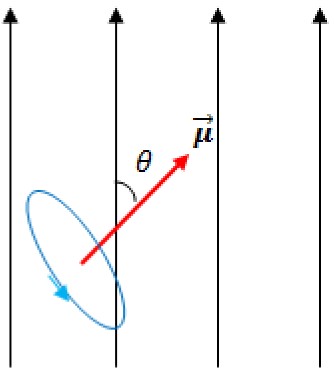
However, one may add the following observation. [We will discuss about the x direction only. Other directions can be included in a similar way.] In free space, where the translational invariance is valid, the Hamiltonian eigenstate can be written as $\exp(ikx)$, which is observed as the momentum eigenstate, since $p_x = -i\hbar\partial/\partial x$: $p_x \exp(ikx) = \hbar k \exp(ikx)$. Observe that $\exp(ikx)$ and $\exp(-ikx)$ have the same energy eigenvalue. In an infinite potential well, these two states can be mixed to give $\sin(kx) = \frac{e^{ikx} - e^{-ikx}}{2i}$, which can be made to vanish at $x = 0$ and $x = L_x$, as required by the boundary condition. Still the energy value of this new state, $\sin(kx)$, is unchanged from that of e^{ikx} or e^{-ikx} in free space. The only difference is that k cannot be arbitrary – it is now discrete, instead of being continuous!

Hydrogen Atom:

Potential is dependent on r only where $r = \sqrt{x^2 + y^2 + z^2}$. Since r is dependent on x, y, and z, the Hamiltonian of the hydrogen atom is not translationally invariant, but is rotationally invariant. As a result, the linear momentum is not conserved but the angular momentum is conserved. This can be shown that the angular momentum operators, L and Lz have the engenfunctions of Hamitonian:

$$\mathbf{H}\psi_{n,l,m_l} = \boldsymbol{E_n}\psi_{n,l,m_l}$$
$$\mathbf{L^2}\psi_{n,l,m_l} = \boldsymbol{l}(\boldsymbol{l}+\mathbf{1})\hbar^2\psi_{n,l,m_l}$$
$$\mathbf{L_z}\psi_{n,l,m_l} = \boldsymbol{m_l}\hbar\psi_{n,l,m_l}$$

Why Spin?



An electron revolving around a nucleus in an atom can be considered as a minute current loop and has a magnetic field of a magnetic dipole $\vec{\mu}$. In an external $\vec{B}$ (magnetic) field, the potential of the magnetic dipole can be defined as:

$$U = -\vec{\mu} \cdot \vec{B} = \left(\frac{e}{2m}\right)\vec{L} \cdot \vec{B} = \left(\frac{e}{2m}\right) L_z B_z$$

Since $\vec{\mu} = -\left(\frac{e}{2m}\right)\vec{L}$

Why? The magnetic moment of a current loop is

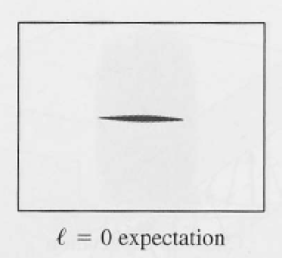
$$\mu = i(\pi r^2) = -e\left(\frac{v}{2\pi r}\right)(\pi r^2) = -e\left(\frac{vr}{2}\right) = -\frac{eL}{2m}$$

The force exerting on the magnetic dipole is

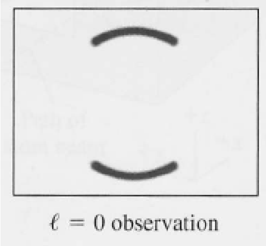
$$F = -\nabla\left(-\vec{\mu} \cdot \vec{B}\right) = -\left(\frac{e}{2m}\right) L_z \frac{\partial B_z}{\partial z}\hat{z} = -\left(\frac{e}{2m}\right)(m_l \hbar)\frac{\partial B_z}{\partial z}\hat{z}$$ where $m_l = -l, \dots, +l$.

$\vec{B} = B_z \hat{z}$ Since $L_z = m_l \hbar$

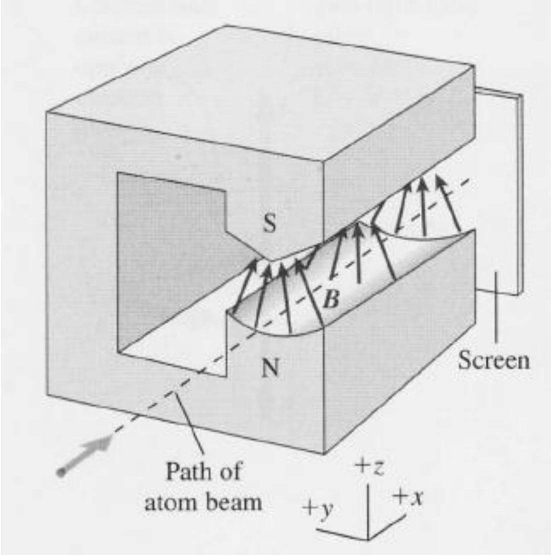
In a uniform $\vec{B}$ field, there is no force exerting on the magnetic dipole. In a non-uniform $\vec{B}$ field, the force varies by m_l.
If l=0 → m_l. = 0 → no orbital motion → no magnetic moment → one spectral line



ℓ = 0 expectation



ℓ = 0 observation



However, the Stern-Gerlach experiment shows that two split lines are present when l=0.

When the spin angular momentum is considered, then the electron in the atomic beam in the experiment can be solved by replacing $-\vec{\mu}$ *with* $\vec{\mu}_s = -\frac{e}{2m}\vec{S}$

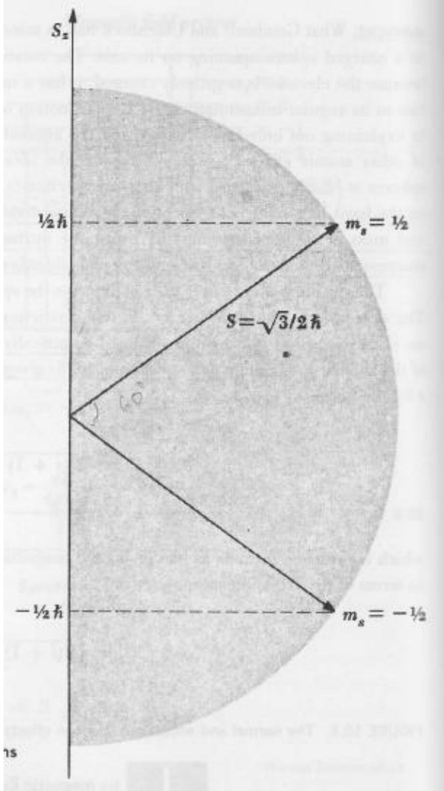
$$F = -\nabla\left(-\vec{\mu} \cdot \vec{B}\right) = -\left(\frac{e}{2m}\right) S_z \frac{\partial B_z}{\partial z}\hat{z} = -\left(\frac{e}{m}\right)(m_s \hbar)\frac{\partial B_z}{\partial z}\hat{z}$$ where $m_s = \pm\frac{1}{2}$ → two lines justified!

To account for this, an intrinsic angular momentum called Spin (S) was introduced by Goudsmit and Uhlenbeck in 1925:

- The intrinsic angular momentum is one of fundamental properties of a particle such as mass and charge.
    - Fermions (Half-integral spin): Electron, proton, neutron, neutrino, and Omega = ½
    - Bosons (integral spin): pion and alpha particle = 0
    - Bosons: Photon, Deutron = 1
- Magnitude of $\vec{S}$, $\overrightarrow{|S|} = \sqrt{s(s+1)}\,\hbar$

  $(e.g.\, electron\ \overrightarrow{|S|} = \frac{\sqrt{3}}{2}\hbar)$
- Direction is quantized by $S_z = m_s\hbar$ where $m_s = -s, .-s+1, \ldots s-1, s$ (e.g. electron -1/2 and 1/2)
- A given particle has intrinsic magnetic dipole moment due to its intrinsic angular momentum:

  $\vec{\mu}_s = g\frac{q}{2m}\vec{S}$ (e.g. electron $\vec{\mu}_s = -\frac{e}{m}\vec{S}$)
- Spin is not classical, so an analogy of rotating its own axis does not properly describe it.
- Now the wave function for the Schrodinger Equation can be completely described using four quantum numbers, n, l, m_l, m_s.



$$\psi_{n,l,m_l,m_s} = \psi_{n,l,m_l}(r,\theta,\phi)m_s$$

OR

$$\psi_{n,l,m_l,+\frac{1}{2}} = \psi_{n,l,m_l}(r,\theta,\phi)\uparrow$$

$$\psi_{n,l,m_l,-\frac{1}{2}} = \psi_{n,l,m_l}(r,\theta,\phi)\downarrow$$

- Spin should increase the degeneracy in the hydrogen atom. The number of states with the same n would increase the degeneracy from n^2 to $2n^2$. But, due to interactions between orbital and spin angular momentums, degeneracy can be broken.
- Photon's Spin is 1. When an atom undergoes a transition in which a photon is produced, there is a limit on how much the atom's angular momentum can change: no more than 1, which creating selection rules for spectral emissions.

Spin-Orbit Coupling (Spin-Orbit Interaction) OR LS Coupling

In a weak external magnetic field where the external magnetic field does not overwhelm the magnetic field internal to the atom, we do not observe separate quantization of $\vec{L}\ and\ \vec{S}$. Rather, we observe the combined angular momentum:

Total Angular Momentum ($\vec{J}$) $\vec{J} = \vec{L} + \vec{S}$

$\overrightarrow{|J|} = \sqrt{j(j+1)}\hbar \qquad where\ j = |l - s|, |l - s| + 1, \ldots |l + s| - 1, |l + s|$
$J_z = m_j\hbar$ where $m_j = -j, -j + 1, \ldots, j - 1, j$
$J_z = L_z \pm S_z$
$m_j\hbar = m_l\hbar + m_s\hbar$

$|\vec{L}| = \sqrt{l(l+1)}\hbar \qquad where\ l = 0, 1, 2, \ldots n - 1$
$L_z = m_l\hbar \qquad where\ m_l = -l, -l + 1, \ldots l - 1, l$

$|\vec{S}| = \sqrt{s(s+1)}\hbar \qquad where\ s\ is\ a\ number\ intrinsic\ to\ a\ given\ particle$
$S_z = m_s\hbar \qquad where\ m_s = -s, -s + 1, \ldots s - 1, s$

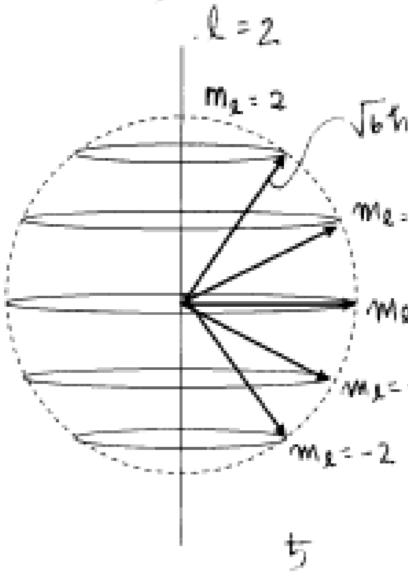
- In a strong magnetic field, LS coupling breaks. In that case, $\vec{L}\ and\ \vec{S}$ are independently quantized.
- Good quantum numbers refer to quantities which can be assigned simultaneously to describe a quantum system at any time. In a weak B field, $n, l, j, m_j\ are\ good\ quantum\ numbers$. In a strong B field, $n, l, m_l, and\ m_s\ are\ good\ quantum\ numbers$.
- The effect of LS coupling is very small compared to the electron energies allowed in the hydrogen atom around 2 x $10^{-5}\ eV$. (compare this with -13.6 eV).--> the effect is observed in the fine structure of hydrogen spectral lines. When L and S are aligned, the energy is slightly higher than when L and S are anti-aligned.

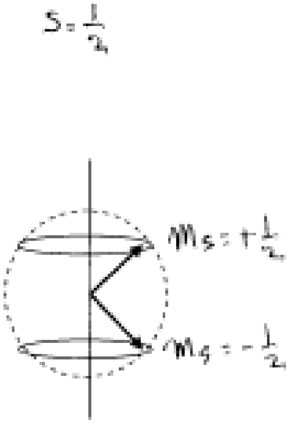
Exercise: Identify the different total angular momentum states possible for $l = 2\ and\ s = \frac{1}{2}$
j can be $l + s\ or\ l - s \rightarrow 2 + \frac{1}{2} \left(= \frac{5}{2}\right)\ or\ 2 - \frac{1}{2}\ (= \frac{3}{2})$

- for $j = \frac{5}{2} \rightarrow m_j = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2} \quad \overrightarrow{|J|} = \sqrt{j(j+1)}\hbar = \sqrt{\frac{5}{2}\frac{7}{2}}\hbar = \frac{\sqrt{35}}{2}\hbar$ → 6 possible states (2*j*+1)
- for $j = \frac{3}{2} \rightarrow m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2} \quad \overrightarrow{|J|} = \sqrt{j(j+1)}\hbar = \sqrt{\frac{3}{2}\frac{5}{2}}\hbar = \frac{\sqrt{15}}{2}\hbar$ → 4 possible states
- A total of 10 states are possible.

If we consider $\vec{L}\ and\ \vec{S}\ separately,$
- For l = 2 → 5 states are possible
- For s = ½ →2 states are possible
- When adding $\vec{L} + \vec{S}$, a total of 5x2 = 10 states are possible. This number agrees to the number of states possible with J.

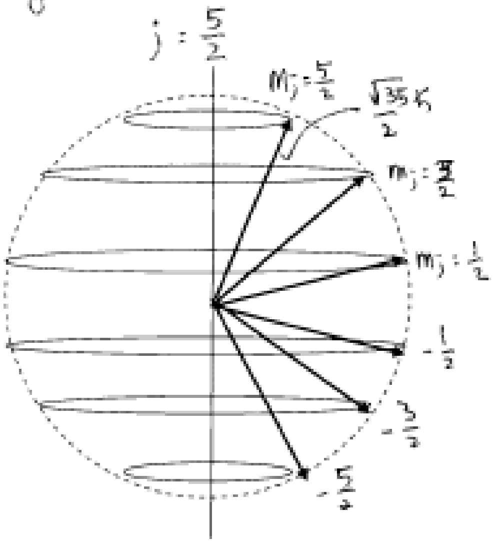
- separate -

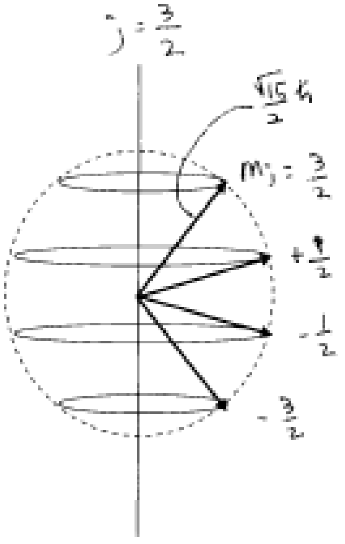




5 × 2 = 10 states

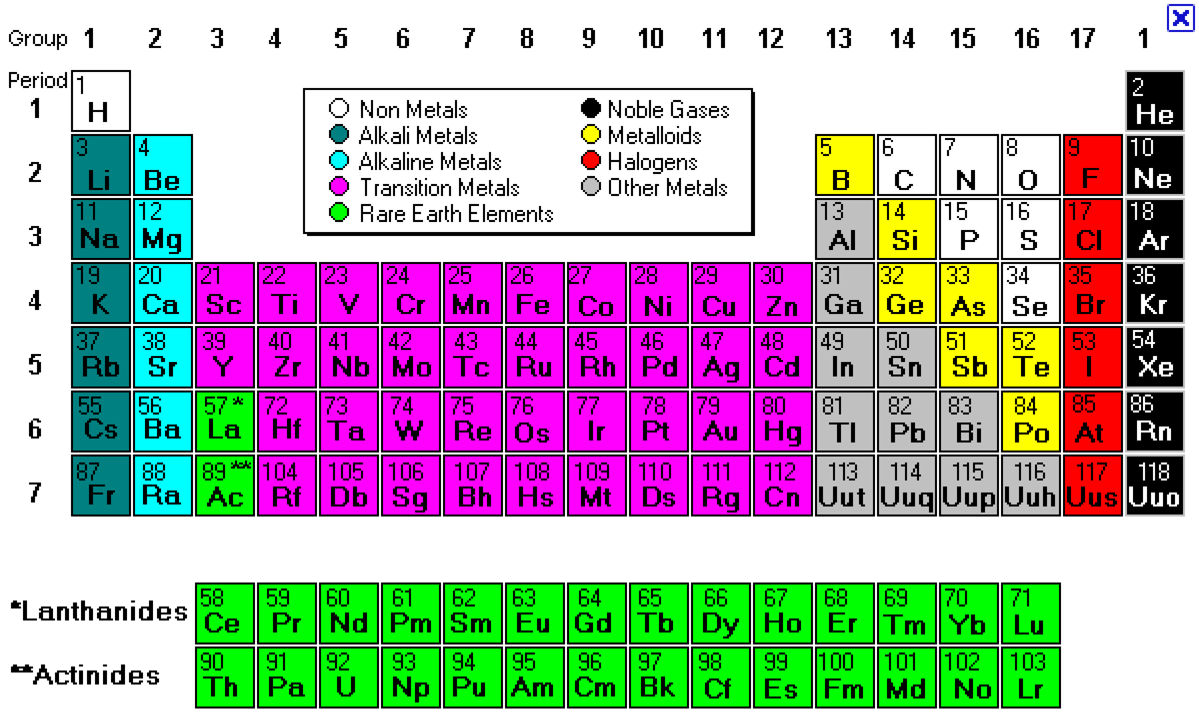
-- LS coupling --





6 + 4 = 10 states

Periodic Table



Group Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	1
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 * La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 ** Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

○ Non Metals
● Alkali Metals
● Alkaline Metals
● Transition Metals
● Rare Earth Elements
● Noble Gases
● Metalloids
● Halogens
● Other Metals

*Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

We need to find out how to put an electron as the atomic number increases in such a way that atoms in a certain group share similar chemical behaviors. If all electrons can occupy the same quantum state, then it is hard to imagine when a small change in the number of electrons gives rise to such distinct chemical behaviors with which we are familiar.

What is known:

- We know how many electrons each atom has
- We know electrons move in orbitals determined by n, l, m_l.
- We know energy level (n) limits what types of orbitals (l) an electron can be in
- We know each l orbital has $2l+1$ possible m_l states for an electron can occupy
- We know an electron has a spin resulting in 2 possible spin states for each of the $2l+1$ possible orbitals. Therefore, for each n, $2n^2$ different states exist.

We need to know rules for

- How to stack electrons across all orbitals → exclusion principle: Pauli, "no two electrons in an atom can exist in the same quantum state" each electron must have a different set of quantum numbers (n, l, m_l, *and* m_s).
- How to construct wave functions when multiple electrons present surrounding one nucleus → identical particle treatment

Identical Particles

If an electron's wave function is $\psi(1)$, another $\psi(2)$, another $\psi(3)$, etc.
The total wave function of the system of n particles can be represented as
$\psi(1,2,3,\dots n) = \psi(1)\psi(2)\,\psi(3)\,\dots\,\psi(n)$

Let’s consider a two particle system:
Particle 1’s wave function = $\psi(1)$
Particle 2’s wave function = $\psi(2)$

Consider Particles 1 and 2 are identical, there is no difference in probability density when exchanged

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$

There are two ways to satisfy this condition:

$$\psi(1,2) = \psi(2,1)$$
$$\psi(1,2) = -\psi(2,1)$$

Write $\psi(1,2) = \psi(1)\psi(2) \ and \ \psi(2,1) = \psi(2)\psi(1)$

When Particle 1 is in n state and Particle 2 is in n’state

$$\psi_I = \psi_n(1)\psi_{n'}(2)$$

When Particle 2 is in n state and Particle 1 is in n’state

$$\psi_{II} = \psi_n(2)\psi_{n'}(1)$$

We have no way of knowing whether $\psi_I or \ \psi_{II} \ is \ right,$ we combine both wave functions in such a way that meet

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$

$$\psi_{Symmetric} = \frac{1}{\sqrt{2}}[\psi_n(1)\psi_{n'}(2) + \psi_n(2)\psi_{n'}(1)]$$

$$\psi_{Anti-Symmetric} = \frac{1}{\sqrt{2}}[\psi_n(1)\psi_{n'}(2) - \psi_n(2)\psi_{n'}(1)]$$

$\psi_{Symmetric} \ satisfies \ \psi(1,2) = \psi(2,1)$:

$$\psi_{Anti-Symmetric} \ satisfies \ \psi(1,2) = -\psi(2,1)$$

Bosons of which spins are an integer satisfies $\psi_{Symmetric}$

- Systems of bosons are described by wave functions that are symmetric upon the exchange of any pair of bosons.

Fermions of which spins are halfinteger satisfies $\psi_{Anti-Symmetric}$→ Exclusion principle applies.

- When $n = n', \psi_{Anti-Symmetric} = 0$. → this cannot be the case → no two electrons can occupy the same quantum state.
- Systems of fermions are described by wave functions that reverse sign upon the exchange of any pair of electrons.
- The anti-symmetric state has a lower energy because two fermions are farther apart, reducing the repulsive energy between the two.
- The exclusion principle applies only two indistinguishable fermions, that is

  - Particles should be of the same fermion type
  - Share the same space.

Periodic Table

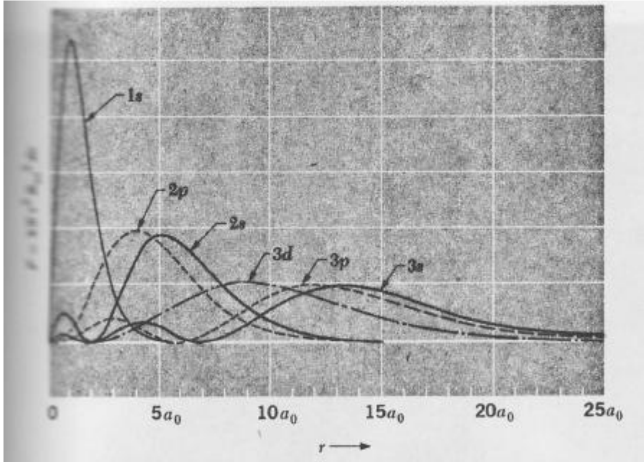
Two basic rules to determine the electron configuration in many-electron atoms:

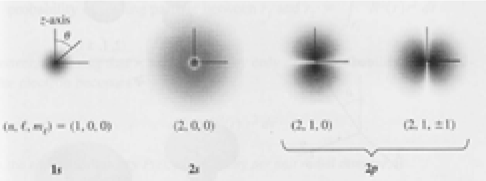
- A system of particles is stable when its total energy is a minimum
- Only one electron can exist in any particular quantum state in an atom (exclusion principle).

Determining what quantum state has lower energy?

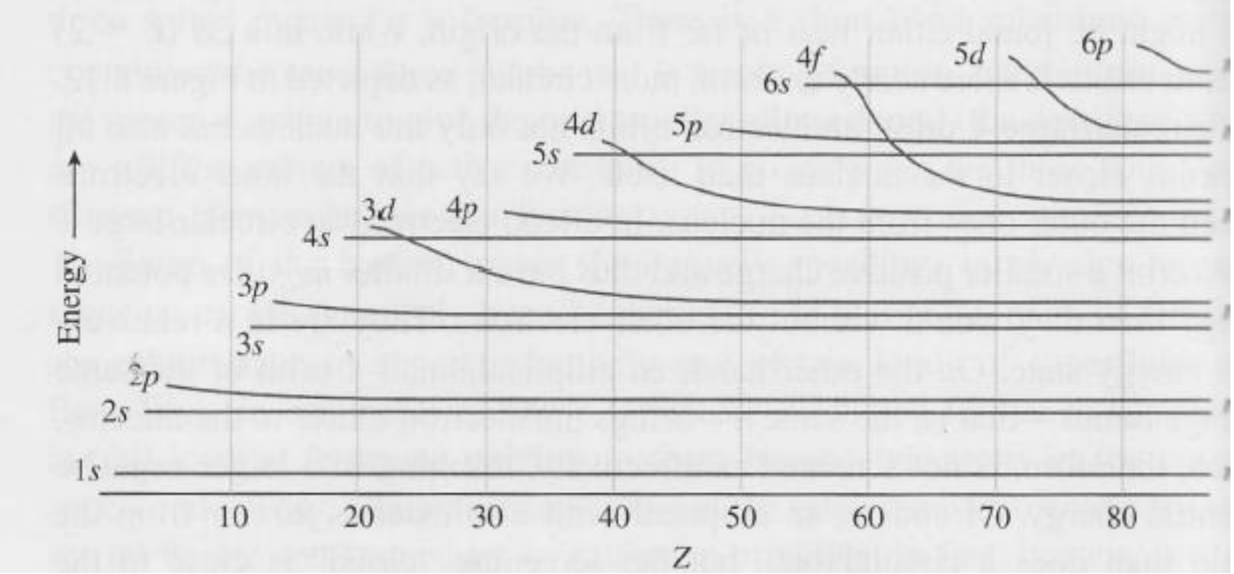
- When *n* is lower.
- With a given *n*, when *l* is lower.

  Why? At a given *n* state, a lower l state has less orbital kinetic energy and more radial energy. Therefore, more anti-nodes exist. This makes the probability density to fluctuate closer to and farther away from the nucleus. Since the Coulomb interaction is proportional to *1/r*, an electron in a lower l state will have a higher probability to get closer to the nucleus where the charge of the nucleus is less shielded by the inner electrons. That increases the magnitude of attractive potential energy, resulting in a lower energy state. This means that the energy of 2*s* is lower than that of 2*p*.





The graph on the next page shows how energy levels align with *l* orbitals in different n states for a given atom (Z = the number of protons/electrons).



- With a given *l*, parallel spin arrangements lower energy.

  Why? Let's consider two electrons in the $2p$ orbital. According to the exclusion principle since electrons are indistinguishable fermions in an atom, the wave function that describes both electrons should be antisymmetric.

When two electrons has a symmetric spin arrangement between electron 1 and electron 2, i.e. $\uparrow\uparrow\ or\ \downarrow\downarrow$, we can write

a wave function where electron 1 occupies *n* state and electron occupies *n'* state:

$$\psi(1,2) = \psi_{n\,n'}(1,2)\uparrow\uparrow$$

If we exchange electron 1 and electron 2, a wave function becomes

$$\psi(2,1) = \psi_{n\,n'}(2,1)\uparrow\uparrow$$

According to the exclusion principle,

$$\psi(1,2) = -\,\psi(2,1)$$

That is

$$\psi_{n\,n'}(1,2)\uparrow\uparrow = -\psi_{n\,n'}(2,1)\uparrow\uparrow$$

$$\psi_{n\,n'}(1,2) = -\psi_{n\,n'}(2,1)$$

If the two electrons are in the same spatial state, $n = n'$, then

$$\psi_{n\,n}(1,2) = -\psi_{n\,n}(2,1) = 0$$

Therefore, the electrons do not occupy the same spatial quantum state. This means that two electrons are farther apart, minimizing the repulsive Coulomb interaction between two electrons. Therefore, the energy is decreased.

If two electrons has an anti-symmetric spin arrangement between electron 1 and electron 2, i.e., $\uparrow\downarrow$, then we can write a wave function where electron 1 occupies n state and electron occupies n' state:

$$\psi(1,2) = \psi_{n\,n'}(1,2)\uparrow\downarrow$$

If we exchange electron 1 and electron 2, a wave function becomes

$$\psi(2,1) = \psi_{n\,n'}(2,1)\downarrow\uparrow$$

According to the exclusion principle,

$$\psi(1,2) = -\,\psi(2,1)$$

That is

$$\psi_{n\,n'}(1,2)\uparrow\downarrow = -\psi_{n\,n'}(2,1)\downarrow\uparrow$$

Since the spin quantum state is already antisymmetric arrangement, i.e. $\uparrow\downarrow = -\downarrow\uparrow$

We can have both electrons can have symmetric spatial quantum state arrangement

$$\psi_{n\,n'}(1,2) = \psi_{n\,n'}(2,1)$$

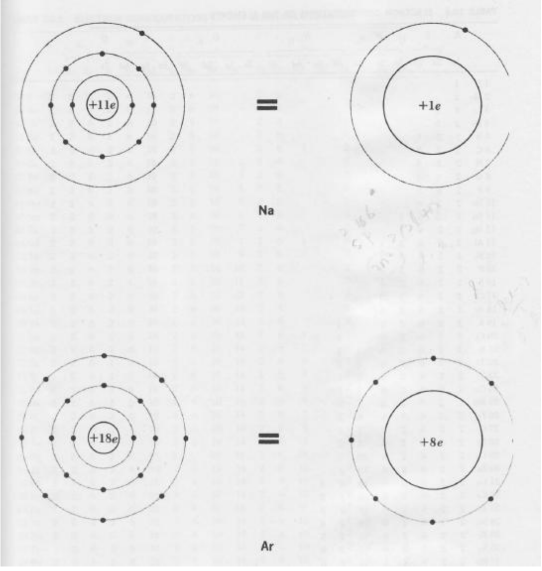
This allows two electrons to be in the same spatial quantum state, which will increase energy.

Therefore, electrons fill the same *l* state symmetrically first until all *l* orbitals are filled.

For example, in filling out *p* orbitals: 3 *p* orbitals to fill:

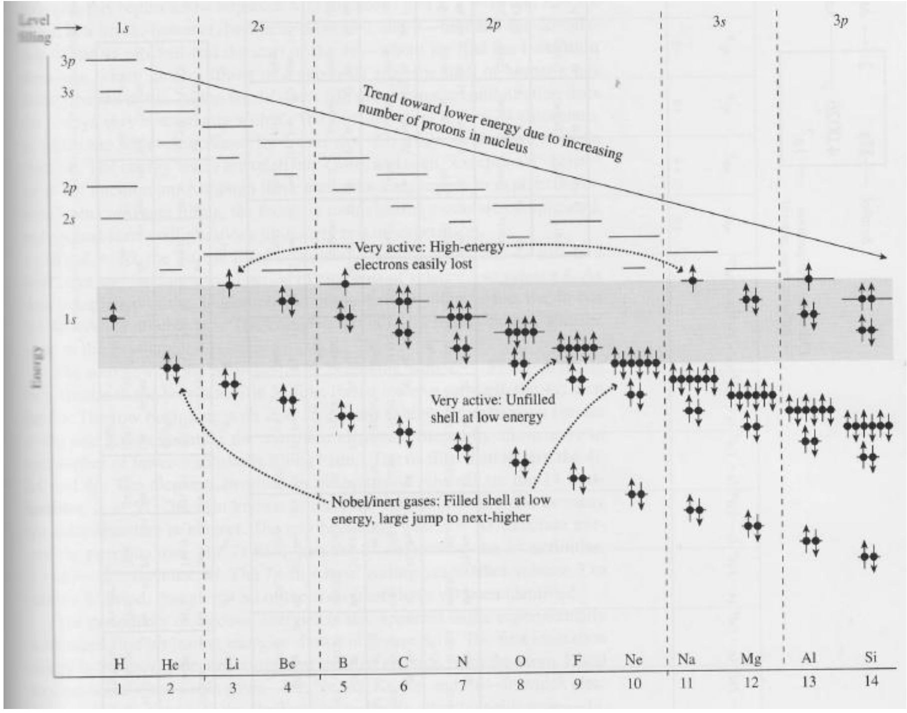
	p_x	p_y	p_z
Lower E	$\uparrow$		
	$\uparrow$	$\uparrow$	
	$\uparrow$	$\uparrow$	$\uparrow$
	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$
Higher E	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

Effective charge of the nucleus due to the screening of inner shell electrons:



Electron shielding in Na and AR atoms. Each outer electron in an Ar atom is acted upon by an effective nuclear charge 8 times greater than that acting upon the outer electron in a Na atom, even though the outer electrons in both cases are in the n=3 shell.

- Chemical behaviors are determined by the number of valence electrons (= the number of electrons in the highest energy level allowed in a ground state of an atom).
- Noble gas: He (Z=2, *n*=1 shell filled), Ne (Z=10, *n*=2 shell filled), Ar (Z=18, *n*=3, 3s and 3p shell filled), Kr (Z=36, 3s, 3p, 3d, 4s, 4p filled), Xe (Z=54, 4s, 4p, 4d, 5s and 5p filled), Rn (Z=86, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 6s, 6p filled). Chemically inert.
- When there is one valence electron exists or one vacancy exists in the outermost shell, atoms become vey active.
- As Z increases, the Coulomb interaction increases between the nucleus and the electrons, resulting in deeper energy levels (lower energy levels).



- Ionization energy: how much energy is necessary to take out one electron from an atom. It is very difficult to get rid of an electron when the shell is filled. It is very easy when fewer electrons exist in the outermost shell.

Figure 8.16 First ionization energies of the elements.